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Water reuse: > 90% water yield in MBR/RO through concentrate recycling and CO₂ addition as scaling control

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ABSTRACT

Over 1.5 years continuous piloting of a municipal wastewater plant upgraded with a double membrane system (ca. 0.6 m³ d⁻¹ of product water produced) have demonstrated the feasibility of achieving high water quality with a water yield of 90% by combining a membrane bioreactor (MBR) with a submerged ultrafiltration membrane followed by a reverse osmosis membrane (RO). The novelty of the proposed treatment scheme consists of the appropriate conditioning of MBR effluent prior to the RO and in recycling the RO concentrates back to the biological unit.

All the 15 pharmaceuticals measured in the influent municipal sewage were retained below 100 ng L⁻¹, a proposed quality parameter, and mostly below detection limits of 10 ng L⁻¹. The mass balance of the micropollutants shows that these are either degraded or discharged with the excess concentrate, while only minor quantities were found in the excess sludge. The micropollutant load in the concentrate can be significantly reduced by ozonation. A low treated water salinity (<10 mM inorganic salts; 280 ± 70 μS cm⁻¹) also confirms that the resulting product has a high water quality.

Solids precipitation and inorganic scaling are effectively mitigated by lowering the pH in the RO feed water with CO₂ conditioning, while the concentrate from the RO is recycled to the biological unit where CO₂ is stripped by aeration. This causes precipitation to occur in the bioreactor bulk, where it is much less of a process issue. SiO₂ is the sole exception. Equilibrium modeling of precipitation reactions confirms the effectiveness of this scaling-mitigation approach for CaCO₃ precipitation, calcium phosphate and sulfate minerals.

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1. Introduction

Water of high quality and in sufficient quantities is an increasingly crucial resource for urban and decentralized

human settlements. While seawater desalination represents a solution for coastal regions, water reuse is a cheaper solution in most cases due to its lower energy requirement (Bartels et al., 2005; Van Houtte and Verbaauwhede, 2008) and is also

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feasible at landlocked locations. The achieved quality, the acceptability of the product water and the overall treatment costs are paramount for the applicability of reuse schemes. The acceptability will not be further discussed here, since non-potable reuse is mostly dominated by cost competitiveness and potable reuse is mostly given if no alternative water resources are available (Anonymous, 2009; Lahnsteiner and Lempert, 2007). In terms of quality, a multi-barrier approach is typically required, and the pathogen, micropollutant and salinity rejection capacity is relevant. It is not a simple matter to discuss the overall cost competitiveness of treatment alternatives, due to the complexity of the processes involved, the multitude of (potential) options for optimization and the diverse influence of local conditions. Investment, maintenance, chemical and energy requirements and the disposal of residuals such as sludge and concentrate are considered to determine the costs of membrane-based systems.

The present article discusses the water quality achievable with dual membrane systems. This treatment scheme is applied today at full scale for potable or high quality industrial reuse e.g. in Singapore and in Belgium (Bartels et al., 2005; Van Houtte and Verbaughede, 2008). In the present study the RO concentrate discharge is significantly reduced thanks to its recycle to the biological unit. Reliable pathogen removal by dual membrane systems has been shown and is not discussed further here (Comerton et al., 2005). The quality of the product water is discussed by presenting mass balances for organic micropollutants and inorganic ions.

Pharmaceuticals, bisphenol A and the anticorrosive benzotriazoles were chosen as representatives of relatively small and often charged contaminants that are quite resistant to biodegradation and are most likely to pass through membranes. Nitrosamines (such as NDMA) were also included in the study since these are formed during chloramination of surface water and wastewater (Schreiber and Mitch, 2006a; Zhao et al., 2008).

Due to scaling on the RO membrane, the fate of inorganic ions is crucial for the feasible water yield, i.e. the amount of product water. The proposed treatment scheme allows controlled precipitation in the biological reactor upstream of the reverse osmosis membrane (RO) by lowering the pH of the feed in the RO with $\text{CO}_{2,\text{aq}}$ and then recycling the RO concentrate back to the MBR where supersaturation is induced by stripping of CO_2 with aeration, leading to salt precipitates in the MBR. It is shown that this allows significant water yields with minimal use of chemicals. The consequent reduction of discarded concentrates represents an advantage, especially at locations where concentrate disposal to the environment is not permitted (e.g. landlocked sites where the concentrate needs to be treated).

2. Materials and methods

2.1. Treatment scheme

Fig. 1 and Table 1 give an overview of the treatment scheme and its principal operating parameters. The reactor was fed with municipal wastewater taken directly from the sewers of the town of Dübendorf (Switzerland) after primary treatment

Fig. 1 – Schematic outline of the experimental setup for upgrading municipal wastewater for high quality water reuse. Percent indications show flowrates relative to the influent. Anox: anoxic compartment; Aerob: aerated compartment housing the UF membrane; RO: reverse osmosis unit (see S1 for details); ●: sampling points.

including a screen, a grid chamber and a primary settler. The feeding flow rate of $0.64 \pm 0.24 \text{ m}^3 \text{ d}^{-1}$ was controlled by the performance of the RO. The unit had been operated from March 2008 to November 2009, a total of 1.7 years (614 days). Stable operation of the entire setup was reached after 80 days.

The two-lane MBR was subdivided into an anoxic part of 440 L and an aerobic compartment of 310 L. The sludge was recycled at a flow rate four times the influent flow from the aerobic to the anoxic compartment. The submerged ultrafiltration (UF) hollow-fiber membranes (eight Zenon ZW10 modules totaling 8 m^2) were housed in the aerobic compartment. The cross-flow aeration of the UF membrane sufficed to cover the biological oxygen demand, resulting in a soluble oxygen concentration in the aerobic compartment $>5 \text{ mgO}_2 \text{ L}^{-1}$. The hydraulic residence time was $15 \pm 3.5 \text{ h}$ and the sludge age ca. 95 d. The sludge concentration in the MBR was $5.8 \pm 2.3 \text{ gTSS L}^{-1}$.

The MBR effluent was conditioned in a 20 L buffer tank with chloramine to minimize biofouling of the RO ($10\text{--}15 \text{ gNH}_2\text{Cl m}^{-3}$) and CO_2 to reduce inorganic scaling ($0.8 \text{ kgCO}_2 \text{ m}^{-3}_{\text{permeate}}$; due to the unknown losses to the headspace, the actual CO_2 requirement should be estimated on the basis of the buffering capacity of the MBR effluent). The RO unit (Figure S1) consisted of a single multistage centrifugal pump (dp-Pumps model DPVF2-180) equipped with a frequency modulator for pressure generation and internal recycling, two spiral-wound RO modules (Dow Filmtec NF90-2540)¹ operated in parallel with a 5.2 m^2 surface area and an EWS OS3050 controller (EWS International -Hertogenbosch, Netherlands). The internal recycle was controlled by a Bürkert flow controller type 8650 (Bürkert GmbH, Ingelfingen, Germany). The rather low specific permeate flux of $4.5 \pm 1.8 \text{ L m}^{-2} \text{ h}^{-1}$ was probably due to the RO being operated at only 5 bar and the irreversible fouling caused by inappropriate chemical cleaning strategies employed during the first year of operation. Until day 522, the RO was operated at a high

¹ The NF90 membrane is designated as nanofiltration by the supplier. According to the very high retention of multivalent as well as monovalent ions (Fig. 6), the term reverse osmosis is deemed more appropriate in the present publication.

Table 1 – Operating conditions of the dual membrane setup (n.a. = not available).

	Conductivity [mS cm ⁻¹]	Organic content TOC [mgC L ⁻¹]	pH	Temperature [°C]	Oxygen [mgO ₂ L ⁻¹]
Influent	1.3 ± 0.3	140 ± 40	7.7 ± 0.4	19 ± 2.3	0.0
MBR effluent	3.2 ± 0.6	10 ± 5	8.1 ± 0.3	20 ± 2.3	>5
RO permeate	0.3 ± 0.1	<0.5	5.8 ± 0.5	26 ± 2.7	n.a.
RO concentrate	6.0 ± 0.9	19 ± 9	6.8 ± 0.4	26.5 ± 2.8	n.a.

cross-flow to permeate flux ratio of 80, while this was reduced to 15 afterward to test the impact on permeability.

The RO was operated at a transmembrane pressure (TMP) of 5 to 6 bar with a pressure drop of 1 bar along the module at a cross-flow of $1.9 \pm 0.1 \text{ m}^3 \text{ h}^{-1}$, dropping proportionally with reduced cross-flow. The averaged net permeate flow was $23.4 \pm 9.2 \text{ L h}^{-1}$. The concentrate recycle rate to the biological unit was $29.4 \pm 6.4 \text{ L h}^{-1}$ and the concentrate discharged about $10 \pm 4\%$ of the recycle rate and controlled proportional to the rate of permeate production.

The chemical maintenance is outlined in Table S1. Each cleaning event was composed of two consecutive steps each lasting 20–30 min. The UF was cleaned in situ by intermittent backwashing (30 s every 2 min, 8× consecutively) while submerged in sludge. The cleaning solution for the UF was disposed into the MBR. The RO was cleaned at 0.5 bar TMP by flushing the pressure vessels with cleaning solution, followed by soaking for 20 min at an exchange rate of the chemical solution of 1 L min^{-1} and maximum cross-flow. The spent chemical cleaning solution was discarded.

The permeability was calculated according to Shirazi et al. (2010):

$$k_w = \frac{J_w}{\Delta P - \Delta \pi} \quad (1)$$

where k_w is the permeability in $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, J_w the measured specific flux in $\text{L m}^{-2} \text{ h}^{-1}$, ΔP the transmembrane pressure in bar and $\Delta \pi$ the osmotic pressure difference over the membrane in bar. The osmotic pressure of the concentrate was calculated from the conductivity measurement according to the correlation shown in Figure S2, obtained by direct measurement during the experimental phase.

The ozonation reactor consisted of a bubble column of 2 m (diameter 63 mm, volume 6 L) operated at an HRT of 0.5–1.5 h. The concentrate of the RO was fed from the top (countercurrent bubble column). The effluent of the ozonation column was recycled to the anoxic compartment of the biological unit. The concentrate discharge occurred prior to the ozonation column. An ozone generator of type Chemodata 1.0 g/Hmax (Chemonorm AG, Altendorf, Switzerland) fed with pure oxygen provided an ozone dose of 5 and $16 \text{ gO}_3 \text{ m}^{-3}_{\text{permeate}}$ corresponding to 0.25 and $0.85 \text{ gO}_3 \text{ gDOC}$, and hence within the typical range for micropollutant removal of secondary effluent. The off-gas was confirmed to be ozone free by online measurement provided by a BMT 964 ozone analyzer (BMT Messtechnik GmbH, Stahnsdorf, Germany). The ozonation column was operated from day 259 to 381.

The reactor was controlled by a Simatic S7 programmable logical controller (Siemens, Germany) and operated via a PC-

based SCADA user interface (CitectSCADA, Schneider Electric, Australia) storing process data every 10 s. The data was evaluated with Matlab (Mathworks, USA).

2.2. Analysis and sampling of micropollutants

The investigated micropollutants were present in the original municipal wastewater and no spiking was performed.

Fig. 1 illustrates the locations of the sampling points. The micropollutant sampling was performed with flow-proportional samplers cooled at 4 °C with a maximum sampling interval of ≤ 30 min. Each sampling campaign was composed of 5 consecutive 24 h composite samples analyzed separately. The sampling campaigns were performed from October 20 to 25, 2008 (without ozonation; operation day 234–239) and from March 9 to 14, 2009 (with ozonation; operation day 374–379). For nitrosamines, three consecutive 24 h composite samples were analyzed (without ozonation November 5–7 2008; with ozonation December 9–11 2008).

The sample analysis for micropollutants was performed by online solid phase extraction (Oasis HLB, Strata XCW/XAW, ENV+) and LC-MS/MS on a Thermo Electron TSQ Quantum Ultra (Hollender et al., 2010). Nitrosamines were analyzed by offline SPE (Oasis HLB above Bakerbond Carbon) and LC-high resolution MS/MS (LTQ orbitrap; Krauss and Hollender, 2008). The quantification limits for micropollutants were around 10 ng L^{-1} in general and between 0.8 and 3 ng L^{-1} for the nitrosamines.

The variation ranges of the influent and product water concentrations over the five days (Figs. 2 and 3) were used as a measure of the typical variation in the measured values.

Contaminant mass flows were calculated by multiplying the measured compound concentration of each sample with the respective daily flow volume. The daily volumetric flows of permeate, excess sludge, concentrate discharge and concentrate recycle were obtained by evaluating the online data measurement (logged at 10 s intervals by the SCADA), with the influent volume calculated as the sum of all outputs (permeate, excess sludge and concentrate). The MBR volume was constant, so changes in the soluble compound mass stored in the reactor volume were calculated from measured concentrations. The accuracy of the mass balances (Figs. 4 and 5) was estimated by Monte Carlo analysis according to Ternes and Joss (2006), assuming a 10% standard error for flow measurements and 20% for the analytical measurement of the compound concentration. Both errors were assumed to be normally distributed. The represented accuracy corresponded to the standard deviation of the results from 5000 Monte Carlo simulation runs.

Fig. 2 – Comparison of micropollutant concentration in the influent municipal wastewater (no spiking) and in the product water without ozonation of the recycled concentrate. The error bars indicate the standard deviation of the five sampled days (days 234–239).

2.3. Analysis and sampling of inorganic ions and precipitates

Inorganic carbon (TIC) was measured with an analyzer model TOC/TIC Analyzer IL 550 (Hach-Lange, Germany).

Anions (Cl^- , SO_4^{2-} , PO_4^{3-} and NO_3^-) were measured with an ion chromatograph model Metrohm 881 Compact IC with a separation column Metrosep A Supp 4 (Metrohm AG, Switzerland). Cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) with an inductively coupled plasma atomic emission spectroscopy

Fig. 3 – Comparison of micropollutant concentration in the influent municipal wastewater (no spiking) and in the product water with ozonation of the recycled concentrate ($0.85 \text{ gO}_3 \text{ g}_{\text{DOC}}^{-1}$). The error bars indicate the standard deviation of the five sampled days (days 374–379).

Fig. 4 – Micropollutant mass balance over the entire sampling campaign of five days without ozonation. Error bars indicate the accuracy for each fraction as estimated by Monte Carlo analysis (sampling days 234–239).

model IC OES-Ciros (Spectro Analytical Instruments GmbH, Germany).

The mass balance of the major ion species (Cl^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} and Si) was determined from 15 consecutive 24 h composite samples starting on May 6, 2009 (day 432–446).

Elemental analysis was performed on 2–3 cm² membrane using X-ray fluorescence (Spectro Xepos+, Kleve, Germany). For that purpose the spiral-wound RO module was dissected and 5 g of the membrane were pressed into 32 mm pellets. Background concentrations were obtained from

Fig. 5 – Micropollutant mass balance over the entire sampling campaign of five days with ozonation (0.85 gO₃ g_{DOC}⁻¹). Error bars indicate the accuracy for each fraction as estimated by Monte Carlo analysis (sampling days 374–379).

measurements of blank membranes and the measurements of the used membranes were corrected accordingly.

2.4. Saturation indices

The PhreeqC simulation software package (Parkhurst and Appelo, 1999) with an associated standard thermodynamic database (*phreeqc.dat*) was used to model the precipitation reactions. Saturation indices (SI) were calculated by the simulation package as follows:

$$SI = \log IAP - \log K \quad (2)$$

where the ionic activity product IAP is the product of ion activities involved in the dissociation equation, and K is the temperature-dependent equilibrium constant. Positive SI values were taken to indicate oversaturation (precipitants will form and scaling can occur), zero indicated equilibrium (no precipitation) and negative values showed under-saturation (precipitants will dissolve).

The solubility constant for vaterite (CaCO_3) of $\log K = -7.91$ given by Sawada (1997) was added to the model database.

The error in the charge balance of the modeled mixtures (Table 3) was always <7% of the total ionic strength, thus in the range of the expected analytical accuracy.

3. Results and discussion

3.1. Removal of micropollutants

Most organic micropollutants are degraded and/or retained to below the detection limit ($\leq 10 \text{ ng L}^{-1}$) by RO, except for small and polar compounds such as the anticorrosive benzotriazoles, as well as some rather persistent pharmaceuticals, namely propranolol, diclofenac and carbamazepine (Figs. 2 and 3). This is in good agreement with the available literature (Hollender et al., 2009; Joss et al., 2005; Radjenovic et al., 2008). A comparison of the concentrations in the concentrate and permeate shows that high retention was achieved by RO. All measurable concentrations are further reduced by inserting an ozonation step in the concentrate recycle loop (Fig. 1).

Table 2 – Elemental analysis (XRF) of the precipitations found on the RO membrane at the end of the experiments (21 samples).

Element	Amount $\text{mg m}^{-2}_{\text{membrane}}$
Ca	16,500 $\pm$ 5,400
Si	850 $\pm$ 440
P	430 $\pm$ 180
Mg	360 $\pm$ 180
Al	224 $\pm$ 143
Fe	144 $\pm$ 47
Zn	106 $\pm$ 31
Sr	33 $\pm$ 10
Cu	14 $\pm$ 4
Pb	11 $\pm$ 3
Cr	6 $\pm$ 2
Br	2 $\pm$ 1

The mass balance shows that without ozonation the retained compounds are mostly degraded but are also discharged in the concentrate, while the excess sludge contains only a minor part of the load (Fig. 4). According to the accuracy estimation performed with Monte Carlo simulations, the degradation of carbamazepine and primidone is not significant, while some degradation is probable for diclofenac (Joss et al., 2005; Kasprzyk-Hordern et al., 2009). This is speculated to be due either to the very high sludge age (ca. 100 days) or to the exposure to anaerobic conditions in the anoxic tank (enhanced biological phosphorus removal was observed; data not shown). The reason why for some compounds the sum of all effluents resulted significantly higher than 100% (i.e. benzotriazoles, carbamazepine, primidone and propranolol) is suspected to be due to underestimation of the influent load due to matrix effects (i.e. systematic errors not accounted for in the accuracy estimation).

Fig. 5 shows that an ozone dose of $0.85 \text{ gO}_3 \text{ gDOC}^{-1}$ effectively eliminates the micropollutants and reduces the discharged amount in the concentrate. Since the DOC concentrations are high in the concentrate, a relatively high ozone dose is required to achieve good elimination of micropollutants. However, the elimination rates obtained were comparable to the results from ozonation experiments on treated municipal wastewater for similar concentrations of ozone relative to DOC (Hollender et al., 2009). Table S2 shows the elimination rates obtained for two ozone doses, and confirms that $0.25 \text{ gO}_3 \text{ gDOC}^{-1}$ is insufficient for substantial removal. A similar setup combining nanofiltration with ozonation had previously been proposed but not tested (Ernst and Jekel, 1999).

Since nitrosamines can be formed from nitrogen-containing precursors during chloramination and ozonation, their concentrations were also measured (Hollender et al., 2009; Krauss et al., 2010). Nitrosamine concentrations in the MBR influent were $15\text{--}32 \text{ ng L}^{-1}$ for NDMA, and $4\text{--}22 \text{ ng L}^{-1}$ for NMOR, and generally below 10 ng L^{-1} for the other nitrosamines. These levels indicate a rather low level of nitrosamine load typical for Swiss wastewater. The NDMA elimination rates in the MBR were 36 and 64% for treatment without respectively with ozonation, those of the other nitrosamines between 20 and 100% and thus in the range of elimination rates reported for lower ng L^{-1} levels in the studies cited above.

The addition of $10\text{--}15 \text{ mg L}^{-1}$ chloramine did not result in a significant formation of NDMA, while up to 23 ng L^{-1} of N-nitrosomorpholine and up to 12 ng L^{-1} of other nitrosamines (N-nitrosopiperidine, N-nitrosodiethylamine and N-nitrosodibutylamine) were formed. The average rejection of NDMA by the RO membrane was about 80% and those of the other nitrosamines between 70 and close to 100%, reducing permeate concentrations below 7 ng L^{-1} for NDMA, below 24 ng L^{-1} for NMOR, and below or close to the limit of quantification ($<3 \text{ ng L}^{-1}$) levels for the other nitrosamines. These values indicate that nitrosamines are rejected to some extent, but not completely by reverse osmosis as reported by Steinle-Darling et al. (2007). Nevertheless, NDMA concentrations in the permeate were already lowered below the interim maximum acceptable concentration of 9 ng L^{-1} for drinking water established by the Ontario Ministry of Environment (OMot, 2003) and were close to the public health goal of

Table 3 – Water composition as measured in 15 samples taken between May 6 and 20, 2009 (days 432–446) is indicated as average $\pm$ standard deviation. The saturation index is given for all compounds that may potentially precipitate in the process based on the modeling of the ion composition. *: in the model pH and total inorganic carbon (TIC) concentrations have been changed for the concentrate to represent typical operating conditions rather than the specific conditions measured during the observation period when the pH was inappropriately high (7.4 ± 0.3).

		Influent wastewater	Wastewater + recycle	MBR effluent	Permeate	Concentrate
Flow	L h ⁻¹	26.1 $\pm$ 3.8	45 $\pm$ 6.5	44.6 $\pm$ 6.5	23 $\pm$ 1.7	2.7 $\pm$ 0.7
Temperature	°C	18 $\pm$ 0.6	20.6 $\pm$ 1	20.6 $\pm$ 0.8	26.2 $\pm$ 1.0	24.6 $\pm$ 1.0
pH		7.4 $\pm$ 0.5	8.1 $\pm$ 0.1	8.2 $\pm$ 0.1	6.2 $\pm$ 0.2	6.8*
TIC	mgC L ⁻¹	107 $\pm$ 15	233 $\pm$ 19	191 $\pm$ 22	16 $\pm$ 2.5	360*
Cl ⁻	mgCl L ⁻¹	138 $\pm$ 25	472 $\pm$ 13	465 $\pm$ 34	27 $\pm$ 4	930 $\pm$ 170
Na ⁺	mgNa L ⁻¹	125 $\pm$ 20	365 $\pm$ 16	352 $\pm$ 35	36 $\pm$ 4	693 $\pm$ 60
K ⁺	mgK L ⁻¹	14.6 $\pm$ 1.4	36 $\pm$ 1	35.5 $\pm$ 3.1	3.6 $\pm$ 0.3	65 $\pm$ 7
Ca ²⁺	mgCa L ⁻¹	118 $\pm$ 16	277 $\pm$ 7	248 $\pm$ 18	1.5 $\pm$ 0.3	494 $\pm$ 52
Mg ²⁺	mgMg L ⁻¹	20.4 $\pm$ 1.6	66 $\pm$ 3	63 $\pm$ 6	0.4 $\pm$ 0.1	127 $\pm$ 15
SO ₄ ²⁻	mgS L ⁻¹	37 $\pm$ 7	133 $\pm$ 4	132 $\pm$ 11	1.6 $\pm$ 0.2	263 $\pm$ 35
Silica species	mgSi L ⁻¹	6.7 $\pm$ 0.6	17.6 $\pm$ 0.6	17 $\pm$ 2	0.8 $\pm$ 0.2	32 $\pm$ 3.5
PO ₄ ³⁻	mgP L ⁻¹	2.3 $\pm$ 0.5	2.7 $\pm$ 0.1	1.7 $\pm$ 0.7	0.1	3.1 $\pm$ 1.1
NO ₃ ⁻	mgN L ⁻¹	<1	2.2 $\pm$ 0.2	2.6 $\pm$ 1.9	0.5 $\pm$ 0.3	4.1 $\pm$ 1
Saturation indices						
Calcite	CaCO ₃	0.5	1.8	1.7	-3.4	0.8
Aragonite	CaCO ₃	0.3	1.6	1.6	-3.6	0.6
Vaterite	CaCO ₃	0	1.2	1.2	-4.0	0.2
Dolomite	CaMg(CO ₃) ₂	0.5	3.2	3.2	-7.0	1.3
Hydroxyapatite	Ca ₅ (PO ₄) ₃ OH	4.3	8.2	7.8	-14	3.6
Chalcedony	SiO ₂	0	0.4	0.4	-1	0.6
Quartz	SiO ₂	0.5	0.8	0.8	-0.6	1.1
Chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	-6.0	0.5	1	-19	-5.6
Sepiolite	Mg ₂ Si ₃ O _{7.5} OH·3H ₂ O	-3.9	0.9	1.3	-14	-2.9
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	-2.3	4.9	5.4	-17	-0.7

3 ng L⁻¹ of California (COoEHH, 2006). Ozonation of the reverse osmosis concentrate resulted in a slight, but not statistically significant increase of NDMA concentrations, while other nitrosamines were not formed.

Overall, the low micropollutant content in the product water confirms the suitability of the treatment scheme for many reuse purposes (e.g. potable or industrial with high quality requirements), with or without concentrate ozonation.

3.2. Salt retention and precipitation

The average RO permeate conductivity of $280 \pm 70 \mu\text{S cm}^{-1}$ is significantly below that of the raw wastewater at $1300 \pm 300 \mu\text{S cm}^{-1}$ (Table 1). Monovalent ions are retained at >70% relative to the influent concentration while all multivalent ions are retained and reduced to $\leq 2 \text{ mg L}^{-1}$ in the permeate (Table 3). Thus, the product water would also be considered as suitable for unrestricted reuse in terms of its salinity (e.g. potable reuse).

The RO concentrate has a conductivity of $6000 \pm 900 \mu\text{S cm}^{-1}$ with HCO₃⁻, Na⁺, Cl⁻, NO₃⁻, K⁺, Ca²⁺, Mg²⁺, SO₄²⁻ and silicates are the dominant ions.

Table 2 lists elemental compositions of the bulk precipitations found on the RO membrane after termination of the experiments (i.e. after 1.7 years of operation) determined with XRF. Calcium is clearly the prevalent element. Si, P and Mg were also present in significant amounts. The other metals were considered of minor importance ($< 10 \text{ mmol m}^{-2}_{\text{membrane}}$).

During the third sampling campaign (from May 6 to 20, day 432 to 446), the concentration of the most significant ions was monitored at the main points of the integrated process, and the average values were used to predict the possible precipitations with the PhreeqC software. Table 3 shows the water composition and the major scalants to be expected according to the saturation indices modeled with highly positive values, i.e. CaCO₃, SiO₂ and magnesium silicates (zero indicates equilibrium, negative saturation indices indicate dissolution of precipitates).

CaCO₃ scaling is a major concern in membrane desalination (AlShammiri and AlDawas, 1997; Pena et al., 2010). It is mostly countered by adding sulfuric acids, hydrochloric acids or anti-scalants prior to RO (Baker et al., 1997; Ning and Netwig, 2002). In the present study, CO₂ addition is used instead of sulfuric acid and the lowering of pH results in a reduction of CO₃²⁻ concentration (in spite of the increase of total inorganic carbon species), and thus a lower saturation index for the carbonate precipitates. This effect was reversed in the biological unit, where CO₂ was removed by stripping with air, the pH increased and significant CaCO₃ precipitation occurred (Figure S3). According to the modeling, a pH of around 6.1 would be required to reach negative saturation indices in the concentrate for all the considered compounds except SiO₂. Nevertheless, according to Lee and Lee (2005), cross-flow allows avoidance of precipitation in spite of a slight oversaturation, so that stable operation may also be achieved at a pH slightly higher than 6.1.

Several studies indicate that calcium phosphate precipitation may be a limiting factor for membrane performance and RO water yield (Bartels et al., 2005; Greenberg et al., 2005; Katz and Dosoretz, 2008; Steiner et al., 2010). Table 3 shows that the treatment scheme also allows the operator to maintain a significantly higher saturation index for hydroxyapatite in the biological unit compared to the membrane compartment, thus driving the precipitation of hydroxyapatite to occur preferentially in the bioreactor. XRF analysis performed on the RO membrane shows P-containing precipitates to be of minor importance (Table 2). According to the modeling of saturation indices a further decrease in pH on the membrane as required for impeding CaCO_3 precipitation should also effectively mitigate hydroxyapatite precipitation.

SiO_2 precipitation cannot be controlled by acid conditioning nor removed via an acid clean. Thus the calculated saturation indices are slightly higher in the RO unit due to the higher Si concentration. Accordingly, it is expected that these precipitates will be a major factor limiting water yield, even if operating at a low pH in the RO feed to avoid significant CaCO_3 precipitation. Magnesium silicate precipitations are expected to occur only at pH values typical for the membrane bioreactor (i.e. $\text{pH} \geq 8$); i.e. dosing Mg into an appropriately configured compartment of the biological unit, so this can potentially result in a sink for SiO_2 .

Contrary to the literature findings (Lee and Lee, 2005), CaSO_4 (anhydrite and gypsum) were not found to be of concern in the present study and were significantly undersaturated in the RO as well as in the bioreactor ($\text{SI} < -0.5$). Since the sulfate content of the influent wastewater was in a typical range ($7\text{--}17 \text{ mgS L}^{-1}$; Tchobanoglous et al., 2003), this study indicates that CaSO_4 precipitation is expected to be

a relevant scalant only if influent concentrations are significantly above that of typical municipal wastewater, e.g. due to intrusion by industrial wastewater or seawater.

The saturation indices on the RO were calculated with the ion concentrations measured in the bulk medium, thus not accounting for the concentration polarization on the membrane. Nevertheless, according to Shirazi et al. (2010) it is estimated that this effect would not change the conclusions drawn under the experimental conditions: the ion concentration on the membrane is estimated to be in the range of 1.2–1.5 times higher than in the bulk solution, thus increasing the saturation indices on the membrane by only 0.2–0.5.

The mass balance of specific ions confirms significant precipitation of CaCO_3 in the MBR sludge or walls (Fig. 6): ca. 30% of the influent Ca^{2+} is accumulated in the MBR as precipitate (Figure S3). The accuracy of the mass balance does not allow recognition of silica precipitation in the RO: the influent and effluent loads correspond well (i.e. no significant silica accumulation in the reactor).

3.3. RO membrane performance

Over the entire experimental period, the unit was operated with an overall water yield of $86.4 \pm 9.3\%$, which corresponds to producing only $12 \pm 7.3\%$ concentrate for disposal. This is about half of what is normally discarded (Bartels et al., 2005; Van Houtte and Verbauwhe, 2008). This confirms that the proposed scheme solves some major scaling issues typically experienced with other installations. Nevertheless, Fig. 7 shows that permeability declines slowly during the experimental period, resulting in a rather low long-term permeability. According to the modeling of the saturation indices as

Fig. 6 – Mass balance of the principal ions. Significant accumulation in the reactor is seen only for Ca^{2+} (effluent load smaller than the influent). All values are expressed as amounts relative to the volume of influent (sampling days 432–446).

Fig. 7 – Permeability of the RO membrane over the entire experimental period calculated according to Eq. (1). From day 391 to day 430 CO₂ dosing was either switched off or significantly lowered. From day 430 onwards, chemical cleaning was performed twice at weekly intervals (Table S1). From day 525 onwards the cross-flow was reduced from 1.7 to 0.5 m³ h^{−1}. Lines show linear regressions of data subsets.

well as the elemental analysis of the deposits on the membrane (Tables 2 and 3), it is assumed that this was mainly due to insufficient CO₂ dosing, since the pH on the RO averaged 7.0 ± 0.4 during the entire study, resulting in significant CaCO₃ precipitation. The observation that increased chemical cleaning of the membrane increased the permeate flux (Fig. 7, from day 430–515) confirms that acid-soluble deposits on the membrane contributed to lowering the permeate flux. It is thus argued that operating the RO at a lower pH value would significantly reduce the decline shown in Fig. 7.

Several studies identify biofouling and microbial growth on the membrane as a major problem (Al-Ahmad et al., 2000; Herzberg et al., 2010). Nevertheless, based on the deposits found on the membrane in this study, it is argued that the decline in permeability shown in Fig. 7 is due primarily to inorganic precipitants. Contrary to reports in the literature (Vrouwenvelder et al., 2010), in this study the permeability loss did not correlate with a pressure drop along the feed channel of the membrane (constantly 1.0 ± 0.1 bar at a cross-flow of 960 ± 60 L h^{−1} and module). This is taken as a further indication that the permeability loss was primarily due to membrane scaling, rather than by biofouling occurring on both membrane and spacer within the feed channel.

It is considered possible that the relatively high dosage of chloramine ($10\text{--}15$ gNH₂Cl m^{−3}) as well as the frequent chemical cleaning of the membrane (weekly) helps to keep biofouling at a low level. The primary scope of the present work was to focus on inorganic scaling under conditions of high water yield. Biofouling was not the focus. Chloramine is typically dosed in the range of $2\text{--}5$ gNH₂Cl m^{−3} and chemical cleaning is performed monthly (Bartels et al., 2005; Van Houtte and Verbauwhe, 2008; Xu et al., 2010). It is acknowledged that an overall optimization of the scheme may allow these biofouling control techniques to be reduced.

3.4. Technical feasibility

The present work shows that conditioning with CO₂ combined with concentrate recycling allows all relevant scalants except SiO₂ to be controlled (the relevance of the latter for the overall performance could not be confirmed, but indirect evidence pointed to the greater significance of other scalants), and thus increasing the water yield.

Assuming that a pH in the range of 6.4–6.5 on the RO is sufficient to avoid significant precipitation (not considering SiO₂), and according to the buffering capacity given by the ion composition in Table 3, conditioning with ca. 2 kgCO₂ m^{−3}_{permeate} is estimated to be required. This quantity of CO₂ coming from a stripping unit must be purified to 50% purity and recycled to the RO unit. The anoxic compartment joining the influent wastewater and concentrate recycles (possibly also the internal sludge recycle) should thus be considered for upgrading to a combined stripping and precipitation unit.

The degree of pH lowering needed in the RO to achieve sustainable operation is regarded as crucial for its economic feasibility. The present study is based purely on the calculation of solubility equilibria. However, several studies have shown that kinetic aspects are actually process-limiting, thus explaining why stable operation may also be feasible for some precipitates with slight oversaturation (Lee and Lee, 2005; Udert et al., 2003). Steiner et al. (2010) showed that this degree of oversaturation depends strongly on the composition of the mixture. The chemical cleaning and cross-flow regime are also considered to be relevant parameters here, besides the pH level in the RO. Finally, the concentrate recycling requires appropriate dimensioning of the UF membrane as well as a reactor configuration amenable to scalant precipitation. It is thus concluded that the economic feasibility of the present treatment scheme can be

assessed only by considering all involved treatment steps and their interdependencies.

4. Conclusion

Double-membrane treatment schemes allow municipal wastewater to be upgraded to a quality suitable for many reuse purposes, with micropollutant concentrations mostly below detection limits of 10 ng L^{-1} and salinity of $<300 \mu\text{S cm}^{-1}$. The formation of nitrosamines as byproducts of chloramination and ozonation was counterbalanced by biological degradation and reverse osmosis rejection resulting in levels below reference limits for NDMA.

The continuous piloting at a water yield of 90% showed that CaCO_3 , hydroxyapatite, $\text{CaMg}(\text{CO}_3)_2$, SiO_2 and Mg-silicates may exceed their solubility concentrations, thus potentially leading to scaling of the RO membrane. Calcium sulfate was always found to be significantly below its solubility limit. Lowering the pH with CO_2 prior to membrane filtration was shown to be highly effective at mitigating inorganic scale formation, but the pH of 6.8 achieved in this study was still shown to be too high to avoid a slow permeability loss due to longer-term inorganic scaling. According to the simulation modeling results, lowering the pH down to between 6.1 and 6.5 should suffice to avoid all relevant precipitations except SiO_2 . The presented treatment scheme was shown to reduce the concentrate discharge by at least a factor of two from the current state of the art, while running with reduced requirements for anti-scalant chemicals.

The present work does not allow the authors to draw conclusions regarding the economic competitiveness of the proposed set-ups compared to other ones, since several optimization options have not yet been thoroughly tested. Among these are the exact pH adjustment required for the RO, the impact of cross-flow, the chemical cleaning strategy and the permeate-to-recycle ratio. Further suitable solutions could be found for properly mixing influent and concentrate in a way allowing the controlled precipitation of salts (i.e. within a controlled crystallization reactor) while stripping CO_2 . Since around $2 \text{ kgCO}_2 \text{ m}^3_{\text{permeate}}$ is estimated to be required, the recycling of the stripped CO_2 back to the RO unit is expected to represent an economic solution at full-scale operation.

Nevertheless, it is argued that at some locations (e.g. continental ones) the reduction of the concentrate volume for disposal by a factor two or more (i.e. from typically 20%–<10% of the treated water) as well as the fact that the scaling control does not produce any salinity increase (i.e. by not involving the addition of sulfuric or hydrochloric acid or other anti-scalants) can be an advantage, thus justifying further research on the applicability of the treatment scheme presented here.

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Appendix. Supplementary data

Supplementary data related to this article can be found online at [doi:10.1016/j.watres.2011.09.011](https://doi.org/10.1016/j.watres.2011.09.011).

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